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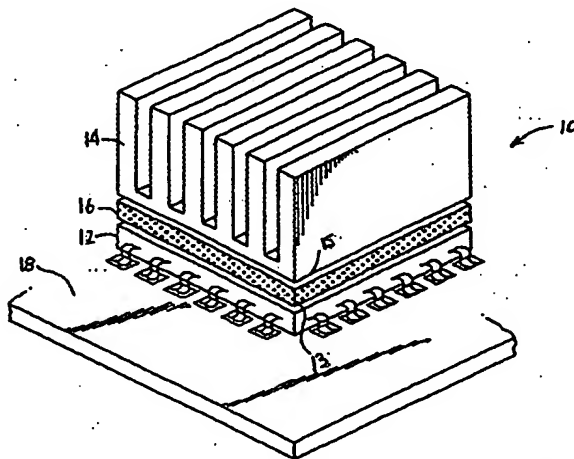
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(54) Title: THERMALLY CONDUCTIVE MATERIALS IN A HYDROPHOBIC COMPOUND FOR THERMAL MANAGEMENT



(57) Abstract: The present invention is directed to a moisture resistant, thermally conductive material (16) comprising a particulate filler comprising thermally conductive particles having a hydrophobic compound coating and a binder effective to join together the filler particles. The present invention also includes an electronic apparatus comprising a heat source (12), a heat sink (14), and a layer (16) of the moisture resistant, thermally conductive interface material disposed between and in contact with the heat source (12) and the heat sink (14). Still, the present invention is directed to a moisture resistant, thermally conductive material comprising particles of agglomerated boron nitride having a hydrophobic compound coating. Yet, the present invention includes a method of removing heat from a heat source comprising providing a heat sink proximate the heat source and disposing a layer of the moisture resistant, thermally conductive material between and in contact with the heat source and the heat sink.

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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## **THERMALLY CONDUCTIVE MATERIALS IN A HYDROPHOBIC COMPOUND FOR THERMAL MANAGEMENT**

### **FIELD OF THE INVENTION**

5           This invention relates to modified thermally conductive powders or particulates having a hydrophobic compound coating on substantially the entire surface thereof which can be used to produce thermally conductive materials.

### **BACKGROUND OF THE INVENTION**

10           Integrated circuit chips are steadily becoming smaller and more powerful. The current trend is to produce integrated chips which are steadily increasing in density and perform many more functions in a give period of time over predecessor chips. This results in an increase in the electrical current used by these integrated circuit chips. As a result, these integrated circuit chips generate more ohmic heat than the predecessor chips. Accordingly, heat management has  
15           become a primary concern in the development of electronic devices.

          Typically, heat generating sources or devices, such as, integrated circuit chips, are mated with heat sinks to remove heat which is generated during their operation. However, thermal contact resistance between the source or device and the heat sink limits the effective heat removing capability of the heat sink.  
20           During assembly, it is common to apply a layer of thermally conductive grease, typically a silicone grease, or a layer of a thermally conductive organic wax to aid in creating a low thermal resistance path between the opposed mating surfaces of the heat source and the heat sink. Other thermally conductive materials are based upon the use of a binder, preferably a resin binder, such as, a silicone, a  
25           thermoplastic rubber, a urethane, or an acrylic, into which one or more thermally conductive fillers are distributed.

          Typically, these fillers are one of two major types: thermally conductive, electrically insulative or thermally conductive, electrically conductive fillers. Aluminum oxide, magnesium oxide, zinc oxide, aluminum nitride, and  
30           boron nitride are the most often cited types of thermally conductive, electrically

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insulative fillers used in thermal products. Boron nitride is especially useful in that it has excellent heat transfer characteristics and is relatively inexpensive.

Unfortunately, certain thermally conductive fillers have a tendency to be hygroscopic. For example, boron nitride is generally regarded as hydrophobic, but it inherently contains the hygroscopic impurity boric oxide ( $B_2O_3$ ). When placed into a humid environment, boric oxide contained within the boron nitride powder or particulates adsorbs atmospheric water. The adsorbed water, in turn, especially in the presence of heat, reacts with boron nitride to form boric acid, a hydrolytic oxidation product of boron nitride and water. Boric acid is also hygroscopic and adsorbs water from the atmosphere to accelerate degradation of the boron nitride particles through this autocatalytic reaction process. Over time, sufficient boron nitride degradation can occur in the powder or particulates due to boric acid production to cause insufficient thermal conductivity between the heat sink and the integrated circuit chip. Heat can then build in the integrated circuit chip and ultimately cause the failure of the integrated circuit chip and its associated electronic device. Thus, there is a need for hydrophobic or moisture resistant boron nitride powder or particulates for use as a filler in a thermally conductive interface material. Further, there is a need for other moisture resistant powders or particulates utilized as thermally conductive filler materials to prevent water contamination and resulting damage to surrounding hardware components. The present invention is directed to overcoming this deficiency in the art.

### SUMMARY OF THE INVENTION

The present invention relates to a moisture resistant, thermally conductive material comprising a particulate filler comprising thermally conductive particles having a hydrophobic compound coating, such as, silicone oil, and a binder effective to join together the filler particles.

Another aspect of the present invention includes an electronic apparatus comprising a heat source, a heat sink, and a layer of a moisture resistant, thermally conductive material made in accordance with the present invention disposed between and in contact with the heat source and the heat sink.

Still, another aspect of the present invention includes a moisture resistant, thermally conductive material comprising particles of agglomerated boron nitride having a hydrophobic compound coating, such as, a silicone oil coating.

5 Yet, another aspect of the present invention includes a method of removing heat from a heat source comprising providing a heat sink proximate the heat source and disposing a layer of the moisture resistant, thermally conductive interface material of the present invention between and in contact with the heat source and the heat sink.

## 10 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a partial, perspective view of a layer of a moisture resistant, thermally conductive material made in accordance with the present invention disposed between an integrated circuit chip and a heat sink.

## DETAILED DESCRIPTION OF THE INVENTION

15 The present invention relates to a moisture resistant, thermally conductive material which comprises a particulate filler comprising thermally conductive particles having a hydrophobic compound coating, such as, a silicone compound coating, and a binder effective to join together the filler particles. In accordance with the present invention, such moisture resistant, thermally  
20 conductive material has a water absorption rate of less than 1.24 parts per million per square centimeter of particle surface area per minute ( $\text{ppm}/\text{cm}^2 \cdot \text{min.}$ ), preferably less than  $0.12 \text{ ppm}/\text{cm}^2 \cdot \text{min.}$ , and a thermal conductivity of at least 0.4 watts/meter  $^{\circ}\text{K}$ , preferably at least 1 watt/meter  $^{\circ}\text{K}$ . Such material can be utilized as a moisture resistant, thermally conductive interface material to assist in heat  
25 transfer between a heat source and a heat sink. Further, the thermally conductive material of the present invention can be provided as a moisture resistant, thermally conductive, and rigid potting compound or circuit board.

There are numerous polymer binders known in the art which are suitable for use with the present invention. Examples of such binders are  
30 disclosed in U.S. Patent Nos. 5,283,542 to Ochiai et al., 5,194,480 to Block et al.,

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5,950,066 to Hanson et al., 5,591,034 to Ameen et al., 5,738,936 to Hanrahan, 5,028,984 to Ameen et al., 5,926,371 to Dolbear, 5,681,883 to Hill et al., 4,869,954 to Squitieri, and 5,660,917 to Fujimori et al., all of which are incorporated herein by reference. Such binders include polyesters, silicone  
5 resins, polyolefins, epoxies, thermoplastics, thermoplastic rubbers, urethane resins, acrylic resins, polyimides, polyamides, waxes, greases, and combinations thereof.

Thermally conductive particulate fillers of the present invention include both thermally conductive, electrically insulative and thermally  
10 conductive, electrically conductive powders and particulates. Such fillers comprise various kinds of powders or particulate materials of porous or non-porous inorganic pigments, organic pigments, pearlescent pigments, carbons, metals, mica, mineral silicates, metal oxides, metal hydroxides, metal borides, metal carbides, metal nitrides, ceramics, carbonate minerals, sulfate minerals,  
15 phosphate minerals, and combinations thereof. Any conventional particle size may be used. Preferably, the particles range in size from about 1  $\mu\text{m}$  to about 500  $\mu\text{m}$ . Further, the filler may contain a mixture of coarse (greater than about 100  $\mu\text{m}$ ) and fine (about 0.001  $\mu\text{m}$  to about 100  $\mu\text{m}$ ) particle sizes. For a compliant material (i.e., flexible or low durometer), such as, a moisture resistant, thermally  
20 conductive interface material, the proportion of filler coated with the hydrophobic compound is from about 5 volume % to about 40 volume % of the moisture resistant material, preferably from about 12 volume % to about 30 volume %. For a substantially rigid, moisture resistant, thermally conductive material, such as, a potting compound or a circuit board, the proportion of filler coated with the  
25 hydrophobic compound is from about 20 volume % to about 70 volume %, preferably from about 50 volume % to about 70 volume %. Thermally conductive materials made in accordance with the present invention can be formed or molded into any desired shape. The thermal conductivity of the thermally conductive material of the present invention has a direct relationship to the amount of filler  
30 contained therein. Accordingly, thermal conductivity of the thermally conductive material of the present invention can be tailored with respect to the amount of filler disposed therein. Suitable thermally conductive powders and particulates

are described in U.S. Patent Nos. 4,801,445 to Fukui et al., which is incorporated herein by reference. Typical examples of such powder materials are explained below.

#### Inorganic pigment

5           Examples of inorganic pigments capable of being modified in accordance with the present invention include, but are not limited to, ultramarine blue (sodium aluminum silicate containing sulfur), prussian blue (ferri ferrocyanide), manganese violet, titanium-coated mica, bismuth oxychloride, iron oxides, iron hydroxide, titanium dioxide, titanium lower oxides, chromium  
10   hydroxide, and combinations thereof.

#### Organic pigment

          Examples of organic pigments capable of being modified in accordance with the present invention include, but are not limited to, C.I. 15850, C.I. 15850:1, C.I. 15585:1, C.I. 15630, C.I. 15880:1, C.I. 73360, C.I. 12085, C.I.  
15   15865:2, C.I. 12075, C.I. 21110, C.I. 21095, C.I. 11680, C.I. 74160 and zirconium, barium, and aluminum lakes of C.I. 45430, C.I. 45410, C.I. 45100, C.I. 17200, C.I. 45380, C.I. 45190, C.I. 14700, C.I. 15510, C.I. 19140, C.I. 15985, C.I. 45350, C.I. 47005, C.I. 42053, and C.I. 42090, and combinations thereof.

#### Pearlescent pigment

20           Examples of pearlescent pigments (or nacreous pigments) capable of being modified in accordance with the present invention include, but are not limited to, mica-titanium composite materials containing as a titanium component titanium dioxide, titanium lower oxides, and titanium oxynitride, mica-iron oxide composite materials, bismuth oxychloride, guanine, and combinations thereof.

#### 25           Carbons

          Examples of carbons capable of being modified in accordance with the present invention include, but are not limited to, activated carbon and carbon black particles conventionally used in, for example, coatings and fillers. Although there are no critical limitations to the sizes of the carbon powder particle, such  
30   carbon powders typically have a particle size of 0.001  $\mu\text{m}$  to 200  $\mu\text{m}$ .

#### Metals

          Examples of metals capable of being modified in accordance with the present invention include, but are not limited to, iron, cobalt, nickel, copper,

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zinc, aluminum, chromium, titanium, zirconium, molybdenum, silver, indium, tin, antimony, tungsten, platinum, gold, and alloys thereof.

#### Mica

Examples of mica capable of being modified in accordance with the present invention include, but are not limited to, muscovite, phlogopite, biotite, sericite, lepidolite, paragonite, artificial or synthetic mica having a fluorine atom substituted for the hydroxyl group of natural mica as well as baked or calcined products thereof. These mica may be used alone or in any mixture thereof.

10

#### Mineral Silicate

Examples of the mineral silicates capable of being modified according to the present invention include, but are not limited to, phyllosilicates, tectosilicates, natrolites, heulandites, and zeolites. Phyllosilicates and tectosilicates include pyrophyllite, talc, chlorite, chrysotile, antigorite, lizardite, kaolinite, dickite, nacrite, halloysite, montmorillonite, nontronite, saponite, sauconite, and bentonite. Natrolites include natrolite, mesolite, scolecite, and thomsonite. Heulandites include heulandite, stilbite, and epistibite. Zeolites include analcite, harmontone, phillipsite, chabazite, and gmelinite. These silicate minerals may be used alone or in combination thereof. The phyllosilicates may have organic cations at the interface of the layers thereof or may be substituted with alkali metal or alkaline earth metal ions. The tectosilicates may include metallic ions in the fine pores thereof.

20

#### Metal Oxide, Hydroxide, Nitride and Oxynitride

Metal oxides, hydroxides, nitrides, and oxynitrides capable of being modified according to the present invention include, but are not limited to, boron, aluminum, silicon, titanium, zirconium, zinc, chromium, magnesium, calcium, iron, manganese, cobalt, nickel, and molybdenum oxides, hydroxides, nitrides, and oxynitrides. Examples of such compounds are magnesium oxide, magnesium hydroxide, calcium oxide, calcium hydroxides, aluminum oxide, aluminum hydroxide, aluminum nitride, boron nitride, silica, silicon nitride, iron oxides ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, FeO), iron hydroxides, titanium dioxide, titanium lower oxides, titanium nitride, zirconium oxide, chromium oxides, chromium hydroxides, chromium nitride, manganese oxides, cobalt oxides, nickel

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oxides, zinc oxides, boron nitride, Si-Al-O-N compounds, Al-O-N compounds, silicon carbide, titanium carbide and tungsten carbide. These oxides, hydroxides, nitrides, and oxynitrides may be used alone or in any mixture thereof.

Furthermore, composite oxides and composite hydroxides such as iron titanate, cobalt titanate, cobalt aluminate also can be used in the present invention.

Composite materials comprising metal oxides, hydroxides, nitrides, or oxynitrides coated on the core materials (e.g., titanium oxides coated mica, iron oxides coated nylon) can also be used in the present invention.

#### Porous Material

In addition to the above-mentioned porous silicate minerals, mica, and metal oxides, examples of other porous materials capable of being modified in accordance with the present invention include, but are not limited to, ceramics and ceramic glasses, such as  $KAl_2(Al, Si_3)O_{10}F_2$ ,  $KMg(Al, Si_3)O_{10}F_2$ ,  $K(Mg, Fe_3)(Al, Si_3)O_{10}F_2$ ; carbonate minerals, such as,  $CaCO_3$ ,  $MgCO_3$ ,  $FeCO_3$ ,  $MnCO_3$ ,  $ZnCO_3$ ,  $CaMg(CO_3)_2$ ,  $Cu(OH)_2CO_3$ ,  $Cu_3(OH)_2(CO_3)_2$ ; sulfate minerals, such as,  $BaSO_4$ ,  $SrSO_4$ ,  $PbSO_4$ ,  $CaSO_4$ ,  $CaSO_4 \cdot 2H_2O$ ,  $CaSO_4 \cdot 5H_2O$ ,  $Cu_4SO_4(OH)_6$ ,  $KAl_3(OH)_6(SO_4)_2$ ,  $KFe_3(OH)_6(SO_4)_2$ ; and phosphate minerals, such as,  $YPO_4$ ,  $(Ce, La)PO_4Fe_3(PO_4)_2 \cdot 8H_2O$ ,  $Ca_5(PO_4)_3F$ ,  $Ca_5(PO_4)_3Cl$ ,  $Ca_5(PO_4)_3OH$ ,  $Ca_5(PO_4)_3CO_3OH$ ,  $(F, OH)$ . These materials may be used alone or in any mixture thereof.

Furthermore, these porous materials may be modified after granulation or molding, followed by baking or calcining.

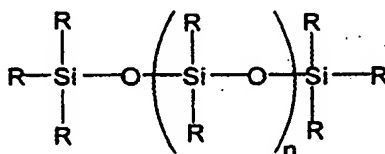
The preferred thermally conductive particles are boron nitride particles, including porous and bonded boron nitride particles. Particularly preferred are agglomerated boron nitride particles. There are several methods known in the art to produce boron nitride. For example, boron nitride can be produced by direct nitriding of borate compounds, such as, boric oxide, boric acid, calcium borates, sodium borates, etc., with an ammonia compound, such as, ammonia and organic amines (e.g., melamine). Boron nitride can also be produced by carbothermic reduction of borate compounds in the presence of nitrogen. Alternatively, boron nitride can be produced by direct nitridation of elemental boron or boron compounds. The boron nitride produced from these methods is typically in the form of a briquette. Boron nitride powder can thereafter be produced by conventional milling. Low density agglomerated boron

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nitride particulates can be made by crushing the briquettes and classifying the agglomerates to target particle size distribution. A method of producing high density agglomerated boron nitride particulates is disclosed in U.S. Patent No. 5,898,009 to Shaffer et al., which is incorporated herein by reference.

5 Silicon nitride and aluminum nitride particulates are also particularly useful with the present invention. Like boron nitride, silicon nitride and aluminum nitride can also be produced by respective carbothermic reduction of silicon and aluminum compounds in the presence of nitrogen. Silicon nitride and aluminum nitride can as well be respectively produced by direct nitridation of  
10 elemental silicon or aluminum compounds. An example of a process for preparing silicon nitride powder is disclosed in U.S. Patent No. 4,514,370, which is incorporated herein by reference.

Hydrophobic compounds utilized in the present invention include silicone compounds, preferably silicone oils. Such silicone oils are low molecular  
15 weight oligomeric siloxanes having the following general structure:



wherein n is 0-5, each R is independently selected from hydrogen, a substituted or unsubstituted alkyl having 1 to 8 carbon atoms, a substituted or  
20 unsubstituted aryl, a substituted or unsubstituted alkene, OR<sup>1</sup>, and OSiR<sup>1</sup>, and each R<sup>1</sup> is independently selected from hydrogen, a substituted or unsubstituted alkyl having 1 to 8 carbon atoms, a substituted or unsubstituted aryl, and a substituted or unsubstituted alkene.

In the preferred embodiment, the siloxane comprises from about 1  
25 to 4 % by weight of the filler. The amount of siloxane varies proportionally with the surface area of the particles. That is, the greater the surface area of the particles, the greater the amount of siloxane needed to coat the particles. Siloxanes well suited for use with the present invention are polydimethylsiloxane,

polymethylhydrogen siloxane, and combinations thereof. For example, polydimethylsiloxane and polymethylhydrogen siloxane preferably comprise about 3 % by weight of the filler when the filler is boron nitride having a particle size of about 5  $\mu\text{m}$ . The siloxane can be coated on the surface of the boron nitride particles in a blender, such as, a ribbon blender, at a temperature between about 20 °C to about 100 °C under either a partial pressure or an inert gas purge. Preferably, the siloxane is introduced into the blender through a spray nozzle, such as, an atomizing nozzle, to produce fine particulates of siloxane.

By substantially coating the entire surface of the particles with the hydrophobic compound, atmospheric moisture is barred from contacting the particles where it can be either absorbed or adsorbed and degrade the thermal conductivity of the thermally conductive material. For example, boron nitride contains the hygroscopic impurity boric oxide. When placed into a humid environment, boric oxide contained within the boron nitride particles adsorbs water. Boron nitride, in turn, especially in the presence of heat, undergoes a hydrolytic oxidation reaction with the adsorbed water to form boric acid. Boric acid is also hygroscopic and further degrades the boron nitride particles through this autocatalytic reaction process through continued water adsorption. Eventually, the thermally conductive material containing the boron nitride filler sufficiently degrades and fails to satisfactorily conduct heat away from a heat source. This can result in failure of the heat source due to heat build-up therein. Also, aluminum nitride is known to hydrolyze slowly in the presence of atmospheric moisture to form aluminum oxide and/or aluminum hydroxide, materials with a substantially lower thermal conductivity than aluminum nitride. A coating of aluminum oxide and/or aluminum hydroxide on the surface of an aluminum nitride particle can act as a thermal diffusion barrier. For this reason it is desirable to minimize contact between the aluminum nitride particles and atmospheric moisture. Even if the particulate material is inert with respect to water, water absorbed by the particulates can react with the materials of adjacent components or act as a thermal barrier to heat transfer from one particulate to another. By coating the surface of the particulates with the hydrophobic compound, water is barred from contacting the particulates and substantially prevents either water adsorption or absorption, which renders the particulates

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substantially hydrophobic. Accordingly, the thermal conductivity of the thermally conductive material of the present invention is maintained regardless of the atmospheric relative humidity.

As previously mentioned, agglomerated boron nitride particles are particularly preferred for the present invention. Thus, another aspect of the present invention is a moisture resistant, thermally conductive material comprising particles of agglomerated boron nitride having the hydrophobic compound coating.

Referring to Figure 1, an electronic apparatus made in accordance with the present invention includes a heat source 12, such as, an integrated circuit chip, and a heat sink 14. A layer 16 of a moisture resistant, thermally conductive interface material made in accordance with the present invention is disposed between and in contact with the heat source 12 and the heat sink 14. The layer 16 of the interface material of the present invention can be formed in a variety of shapes and sizes to fill particular needs. As illustrated, the heat source 12 is mounted to a circuit board 18 made of a moisture resistant, thermally conductive material in accordance with the present invention to further assist in conducting heat away from the heat source 12. The heat source 12, or chip, is operably connected to an electrical source (not shown) and operates conventionally. As heat is generated by the heat source 12, for example, ohmic heat generated during operation of the integrated circuit chip, the heat is conducted from a heat source outer surface 13 across the layer of thermally conductive interface material of the present invention 16 to a heat sink inner surface 15. The heat is thereafter conventionally dissipated to the atmosphere through the heat sink 14, as known in the art. Because the layer of material 16 substantially covers the heat source outer surface 13 and the heat sink inner surface 15, thermal contact resistance is minimized. Importantly, since the layer of thermally conductive material 16 is hydrophobic, the thermal conductivity of the layer 16 is maintained regardless of the atmospheric relative humidity, thereby extending the useful life of the material and the apparatus 10. Further, because the circuit board 18 is likewise moisture resistant and thermally conductive, water contamination in the electronic apparatus 10 is minimized and the heat load on the heat sink 14 is reduced.

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Accordingly, another aspect of the present invention includes an electronic apparatus comprising a heat source, a heat sink, and a layer of the moisture resistant, thermally conductive material of the present invention disposed between and in contact with the heat source and the heat sink. Still, another aspect of the present invention includes an electronic apparatus comprising a heat source and a moisture resistant, thermally conductive circuit board made in accordance with the present invention.

Further, another aspect of the present invention includes a method of removing heat from a heat source comprising providing a heat sink proximate the heat source and disposing a layer of the moisture resistant, thermally conductive interface material of the present invention between and in contact with the heat source and the heat sink.

#### EXAMPLE

Coated and non-coated boron nitride powders were evaluated for hygroscopic affinity in a closed environment at 85 °C, 85 % relative humidity, and ambient pressure for an indicated period of time. The powders were weighted prior to and after moisture exposure to determine the percent increase in weight due to water. The results are reported in Table 1 below.

Table 1.

Avg. Part. Size microns	Coating	% H <sub>2</sub> O abs of BN Filter
5	N/C	1.65 (15 min.)
5	M	0.80 (400 min.)
5	DM	0.08 (10 min.)
7-11	N/C	1.73 (300 min.)
low density agglomerated	N/C	>0.6% (500 min.)

M = Polymethylhydrogen siloxane, trimethylsiloxy end blocked  
DM = Polydimethylsiloxane  
N/C = no coating applied

Although the invention has been described in detail for the purpose of illustration, it is understood that such detail is solely for that purpose, and

variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention which is defined by the following claims.

**WHAT IS CLAIMED:**

1. A moisture resistant, thermally conductive material comprising:  
5 a particulate filler comprising thermally conductive particles having a hydrophobic compound coating and a binder effective to join together the filler particles.
2. The material as claimed in claim 1, wherein the binder is selected from the group consisting of polyesters, polyolefins, epoxies, silicone  
10 resins, thermoplastics, thermoplastic rubbers, urethane resins, acrylic resins, polyimides, polyamides, fluoropolymers, greases, waxes, and combinations thereof.
3. The material as claimed in claim 1, wherein the thermally conductive particles comprise from about 5 vol.% to about 70 vol.% of the  
15 thermally conductive material.
4. The material as claimed in claim 1, wherein the thermally conductive particles are selected from the group consisting of particles of inorganic pigments, organic pigments, pearlescent pigments, carbons, metals, mica, mineral silicates, metal oxides, metal hydroxides, metal borides, metal  
20 carbides, metal nitrides, ceramics, carbonate minerals, sulfate minerals, phosphate minerals, and combinations thereof.
5. The material as claimed in claim 4, wherein the thermally conductive particles are selected from the group consisting of particles of ultramarine blue (sodium aluminum silicate containing sulfur), prussian blue (ferri  
25 ferrocyanide), manganese violet, titanium-coated mica, bismuth oxycchloride, iron oxides, iron hydroxide, titanium dioxide, titanium lower oxides, chromium hydroxide, C.I. 15850, C.I. 15850:1, C.I. 15585:1, C.I. 15630, C.I. 15880:1, C.I. 73360, C.I. 12085, C.I. 15865:2, C.I. 12075, C.I. 21110, C.I. 21095, C.I. 11680, C.I. 74160 and zirconium, barium, and aluminum lakes of C.I. 45430, C.I. 45410,  
30 C.I. 45100, C.I. 17200, C.I. 45380, C.I. 45190, C.I. 14700, C.I. 15510, C.I. 19140,

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C.I. 15985, C.I. 45350, C.I. 47005, C.I. 42053, and C.I. 42090, mica-titanium composite materials containing as a titanium component titanium dioxide, titanium lower oxides, and titanium oxynitride, mica-iron oxide composite materials, bismuth oxychloride, guanine, activated carbon, carbon black, iron and alloys thereof, cobalt and alloys thereof, nickel and alloys thereof, copper and alloys thereof, zinc and alloys thereof, aluminum and alloys thereof, chromium and alloys thereof, titanium and alloys thereof, zirconium and alloys thereof, molybdenum and alloys thereof, silver and alloys thereof, indium and alloys thereof, tin and alloys thereof, antimony and alloys thereof, tungsten and alloys thereof, platinum and alloys thereof, gold and alloys thereof, muscovite, phlogopite, biotite, sericite, lepidolite, paragonite, artificial or synthetic mica having a fluorine atom substituted for the hydroxyl group of natural mica and baked or calcined products thereof, phyllosilicates, tectosilicates, natrolites heulandites, zeolites, magnesium oxide, magnesium hydroxide, calcium oxide, calcium hydroxides, aluminum oxide, aluminum hydroxide, silica, iron oxides, iron hydroxides, titanium dioxide, titanium lower oxides, zirconium oxide, chromium oxides, chromium hydroxides, manganese oxides, cobalt oxides, nickel oxides, zinc oxides, iron titanate, cobalt titanate, cobalt aluminate,  $KAl_2(Al, Si_3)O_{10}F_2$ ,  $KMg(Al, Si_3)O_{10}F_2$ ,  $K(Mg, Fe_3)(Al, Si_3)O_{10}F_2$ ,  $CaCO_3$ ,  $MgCO_3$ ,  $FeCO_3$ ,  $MnCO_3$ ,  $ZnCO_3$ ,  $CaMg(CO_3)_2$ ,  $Cu(OH)_2CO_3$ ,  $Cu_3(OH)_2(CO_3)_2$ ,  $BaSO_4$ ,  $SrSO_4$ ,  $PbSO_4$ ,  $CaSO_4$ ,  $CaSO_4 \cdot 2H_2O$ ,  $CaSO_4 \cdot 5H_2O$ ,  $Cu_4SO_4(OH)_6$ ,  $KAl_3(OH)_6(SO_4)_2$ ,  $KFe_3(OH)_6(SO_4)_2$ ,  $YPO_4$ ,  $(Ce, La)PO_4Fe_3(PO_4)_2 \cdot 8H_2O$ ,  $Ca_5(PO_4)_3F$ ,  $Ca_5(PO_4)_3Cl$ ,  $Ca_5(PO_4)_3OH$ ,  $Ca_5(PO_4, CO_3OH)_3(F, OH)$ , titanium nitride, boron nitride, chromium nitride, aluminum nitride, silicon nitride, Si-Al-O-N compounds, Al-O-N compounds, silicon carbide, titanium carbide, tungsten carbide and combinations thereof.

6. The material as claimed in claim 5, wherein the thermally conductive particles are boron nitride particles.

7. The material as claimed in claim 6, wherein the boron nitride particles are porous boron nitride particles.



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8. The material as claimed in claim 6, wherein the boron nitride particles are bonded boron nitride particles.

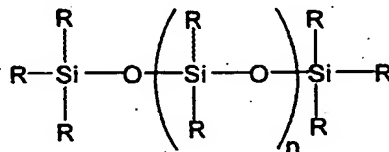
9. The material as claimed in claim 6, wherein the boron nitride particles are agglomerated boron nitride particles.

5 10. The material as claimed in claim 1, wherein the thermally conductive particles range in size from about 0.001  $\mu\text{m}$  to about 500  $\mu\text{m}$ .

11. The material as claimed in claim 1, wherein the hydrophobic compound is a silicone compound.

10 12. The material as claimed in claim 1, wherein the silicone compound is a siloxane.

13. The material as claimed in claim 12, wherein the siloxane has the following general structure:



15

wherein:

n is 0-5;

R and R<sup>1</sup> are independently selected;

R is selected from the group consisting of hydrogen, a substituted or unsubstituted alkyl having 1 to 8 carbon atoms, a substituted or unsubstituted aryl, a substituted or unsubstituted alkene, OR<sup>1</sup>, and OSiR<sup>1</sup>; and

20 R<sup>1</sup> is selected from the group consisting of hydrogen, a substituted or unsubstituted alkyl having 1 to 8 carbon atoms, a substituted or unsubstituted aryl, and a substituted or unsubstituted alkene.

14. The material as claimed in claim 12, wherein the siloxane  
25 comprises from about 1 to about 4 % by weight of the filler.

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15. A moisture resistant, thermally conductive interface material comprising:

the material as claimed in claim 3, wherein the thermally conductive particles comprise from about 5 vol.% to about 40 vol.% of the thermally conductive material.

16. A moisture resistant, thermally conductive potting compound comprising:

the material as claimed in claim 3, wherein the thermally conductive particles comprise from about 20 vol.% to about 70 vol.% of the thermally conductive material.

17. An electronic apparatus comprising:

a heat source and

a circuit board comprising the potting compound of claim 16.

18. An electronic apparatus comprising:

a heat source;

a heat sink for removing heat from the heat source; and

a layer of a moisture resistant, thermally conductive material disposed between the heat source and the heat sink.

19. The apparatus according to claim 18, wherein the thermally conductive interface material comprises:

a particulate filler comprising thermally conductive particles having a hydrophobic compound coating and

a binder effective to join together the filler particles.

20. The apparatus as claimed in claim 19, wherein the binder is selected from the group consisting of polyesters, polyolefins, epoxies, silicone resins, thermoplastics, thermoplastic rubbers, urethane resins, acrylic resins, polyimides, polyamides, fluoropolymers, greases, waxes, and combinations thereof.

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21. The apparatus as claimed in claim 19, wherein the thermally conductive particles comprise from about 5 vol.% to about 70 vol.% of the thermally conductive material.

22. The apparatus as claimed in claim 19, wherein the thermally conductive particles are selected from the group consisting of particles of inorganic pigments, organic pigments, pearlescent pigments, carbons, metals, mica, mineral silicates, metal oxides, metal hydroxides, metal borides, metal carbides, metal nitrides, ceramics, carbonate minerals, sulfate minerals, phosphate minerals, and combinations thereof.

23. The apparatus as claimed in claim 22, wherein the thermally conductive particles are selected from the group consisting of particles of ultramarine blue (sodium aluminum silicate containing sulfur), prussian blue (ferri ferrocyanide), manganese violet, titanium-coated mica, bismuth oxychloride, iron oxides, iron hydroxide, titanium dioxide, titanium lower oxides, chromium hydroxide, C.I. 15850, C.I. 15850:1, C.I. 15585:1, C.I. 15630, C.I. 15880:1, C.I. 73360, C.I. 12085, C.I. 15865:2, C.I. 12075, C.I. 21110, C.I. 21095, C.I. 11680, C.I. 74160 and zirconium, barium, and aluminum lakes of C.I. 45430, C.I. 45410, C.I. 45100, C.I. 17200, C.I. 45380, C.I. 45190, C.I. 14700, C.I. 15510, C.I. 19140, C.I. 15985, C.I. 45350, C.I. 47005, C.I. 42053, and C.I. 42090, mica-titanium composite materials containing as a titanium component titanium dioxide, titanium lower oxides, and titanium oxynitride, mica-iron oxide composite materials, bismuth oxychloride, guanine, activated carbon, carbon black, iron and alloys thereof, cobalt and alloys thereof, nickel and alloys thereof, copper and alloys thereof, zinc and alloys thereof, aluminum and alloys thereof, chromium and alloys thereof, titanium and alloys thereof, zirconium and alloys thereof, molybdenum and alloys thereof, silver and alloys thereof, indium and alloys thereof, tin and alloys thereof, antimony and alloys thereof, tungsten and alloys thereof, platinum and alloys thereof, gold and alloys thereof, muscovite, phlogopite, biotite, sericite, lepidolite, paragonite, artificial or synthetic mica having a fluorine atom substituted for the hydroxyl group of natural mica and baked or calcined products thereof, phyllosilicates, tectosilicates, natrolites, heulandites, zeolites, magnesium oxide, magnesium hydroxide, calcium oxide,

calcium hydroxides, aluminum oxide, aluminum hydroxide, silica, iron oxides, iron hydroxides, titanium dioxide, titanium lower oxides, zirconium oxide, chromium oxides, chromium hydroxides, manganese oxides, cobalt oxides, nickel oxides, zinc oxides, iron titanate, cobalt titanate, cobalt aluminate,  $KAl_2(Al, Si_3)O_{10}F_2$ ,  $KMg(Al, Si_3)O_{10}F_2$ ,  $K(Mg, Fe_3)(Al, Si_3)O_{10}F_2$ ,  $CaCO_3$ ,  $MgCO_3$ ,  $FeCO_3$ ,  $MnCO_3$ ,  $ZnCO_3$ ,  $CaMg(CO_3)_2$ ,  $Cu(OH)_2CO_3$ ,  $Cu_3(OH)_2(CO_3)_2$ ,  $BaSO_4$ ,  $SrSO_4$ ,  $PbSO_4$ ,  $CaSO_4$ ,  $CaSO_4 \cdot 2H_2O$ ,  $CaSO_4 \cdot 5H_2O$ ,  $Cu_4SO_4(OH)_6$ ,  $KAl_3(OH)_6(SO_4)_2$ ,  $KFe_3(OH)_6(SO_4)_2$ ,  $YPO_4$ ,  $(Ce, La)PO_4Fe_3(PO_4)_2 \cdot 8H_2O$ ,  $Ca_5(PO_4)_3F$ ,  $Ca_5(PO_4)_3Cl$ ,  $Ca_5(PO_4)_3OH$ ,  $Ca_5(PO_4, CO_3OH)_3(F, OH)$ , titanium nitride, boron nitride, chromium nitride, aluminum nitride, silicon nitride, Si-Al-O-N compounds, Al-O-N compounds, silicon carbide, titanium carbide, tungsten carbide, and combinations thereof.

24. The apparatus as claimed in claim 23, wherein the thermally conductive particles are boron nitride particles.

15 25. The apparatus as claimed in claim 24, wherein the boron nitride particles are porous boron nitride particles.

26. The apparatus as claimed in claim 24, wherein the boron nitride particles are bonded boron nitride particles.

20 27. The apparatus as claimed in claim 24, wherein the boron nitride particles are agglomerated boron nitride particles.

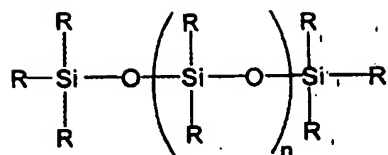
28. The apparatus as claimed in claim 19, wherein the particles range in size from about 0.001  $\mu m$  to about 500  $\mu m$ .

29. The apparatus as claimed in claim 19, wherein the hydrophobic compound is a silicone compound.

25 30. The apparatus as claimed in claim 29, wherein the silicone compound is a siloxane.

31. The apparatus as claimed in claim 30, wherein the siloxane has the following general structure:

- 19 -



wherein:

n is 0-5;

5        R and R<sup>1</sup> are independently selected;

R is selected from the group consisting of hydrogen, a substituted or unsubstituted alkyl having 1 to 8 carbon atoms, a substituted or unsubstituted aryl, a substituted or unsubstituted alkene, OR<sup>1</sup>, and OSiR<sup>1</sup>; and

10        R<sup>1</sup> is selected from the group consisting of hydrogen, a substituted or unsubstituted alkyl having 1 to 8 carbon atoms, a substituted or unsubstituted aryl, and a substituted or unsubstituted alkene.

32.     The apparatus as claimed in claim 30, wherein the siloxane comprises from about 1 to 4 % by weight of the filler.

15        33.     A moisture resistant, thermally conductive material comprising:

particles of agglomerated boron nitride having a hydrophobic compound coating.

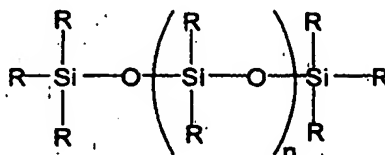
34.     The material as claimed in claim 33, wherein the particles range in size from about 0.001 μm to about 500 μm.

20        35.     The material as claimed in claim 33, wherein the thermally conductive particles comprise from about 5 vol.% to about 70 vol.% of the thermally conductive material.

36.     The material as claimed in claim 33, wherein the hydrophobic compound is a silicone compound.

25        37.     The material as claimed in claim 36, wherein the silicone compound is a siloxane.

38. The material as claimed in claim 37, wherein the siloxane has the following general structure:



wherein:

n is 0-5;

R and R<sup>1</sup> are independently selected;

R is selected from the group consisting of hydrogen, a substituted or unsubstituted alkyl having 1 to 8 carbon atoms, a substituted or unsubstituted aryl, a substituted or unsubstituted alkene, OR<sup>1</sup>, and OSiR<sup>1</sup>; and

R<sup>1</sup> is selected from the group consisting of hydrogen, a substituted or unsubstituted alkyl having 1 to 8 carbon atoms, a substituted or unsubstituted aryl, and a substituted or unsubstituted alkene.

39. The material as claimed in claim 37, wherein the siloxane comprises from about 1 to 4 % by weight of the filler.

40. A method of removing heat from a heat source comprising:  
providing a heat sink proximate the heat source and  
disposing a layer of a moisture resistant, thermally conductive material between and in contact with the heat source and the heat sink.

41. The method according to claim 40, wherein the moisture resistant, thermally conductive interface material comprises:

a particulate filler comprising thermally conductive particles having a hydrophobic compound coating and  
a binder effective to join together the filler particles.

42. The method as claimed in claim 41, wherein the binder is selected from the group consisting of polyesters, polyolefins, epoxies, silicone resins, thermoplastics, thermoplastic rubbers, urethane resins, acrylic resins, polyimides, polyamides, fluoropolymers, greases, waxes, and combinations thereof.

43. The method as claimed in claim 41, wherein the thermally conductive particles are selected from the group consisting of particles of inorganic pigments, organic pigments, pearlescent pigments, carbons, metals, mica, mineral silicates, metal oxides, metal hydroxides, metal borides, metal carbides, metal nitrides, ceramics, carbonate minerals, sulfate minerals, phosphate minerals, and combinations thereof.

44. The method as claimed in claim 43, wherein the thermally conductive particles are boron nitride particles.

45. The method as claimed in claim 44, wherein the boron nitride particles are porous boron nitride particles.

46. The method as claimed in claim 44, wherein the boron nitride particles are bonded boron nitride particles.

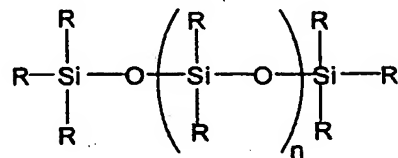
47. The method as claimed in claim 44, wherein the boron nitride particles are agglomerated boron nitride particles.

48. The method as claimed in claim 41, wherein the particles range in size from about 0.001  $\mu\text{m}$  to about 500  $\mu\text{m}$ .

49. The method as claimed in claim 41, wherein the hydrophobic compound is a silicone compound.

50. The method as claimed in claim 49, wherein the silicone compound is a siloxane.

51. The method as claimed in claim 49, wherein the siloxane has the following general structure:



wherein:

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n is 0-5;

R and R<sup>1</sup> are independently selected;

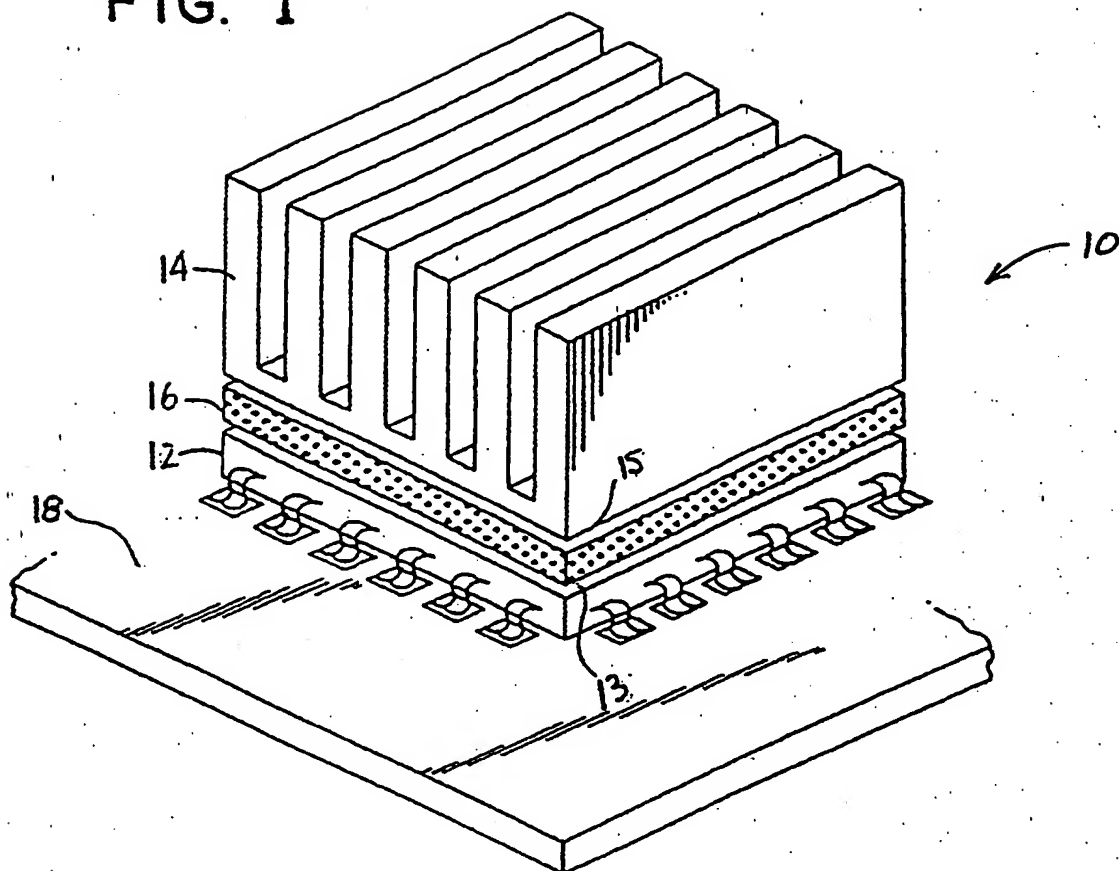
R is selected from the group consisting of hydrogen, a substituted or unsubstituted alkyl having 1 to 8 carbon atoms, a substituted or unsubstituted aryl, a substituted or unsubstituted alkene, OR<sup>1</sup>, and OSiR<sup>1</sup>; and

R<sup>1</sup> is selected from the group consisting of hydrogen, a substituted or unsubstituted alkyl having 1 to 8 carbon atoms, a substituted or unsubstituted aryl, and a substituted or unsubstituted alkene.

52. The method as claimed in claim 50, wherein the siloxane  
10 comprises from about 1 to 4 % by weight of the filler.



FIG. 1



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/25811

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : B32B 5/16; H01L 23/28; H05K 1/03, 3/00

US CL : 428/323, 327, 332, 403, 407, 698, 704; 257/706, 787; 361/748, 751

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/323, 327, 332, 403, 407, 698, 704; 257/706, 787; 361/748, 751

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST 1.2

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,869,954 A (SQUITIERI) 26 September 1989, entire document.	1-52
X	US 5,194,480 A (BLOCK et al) 16 March 1993, entire document	1-52
A	US 5,213,868 A (LIBERTY et al) 25 May 1993, entire document.	1-52
X	US 4,882,225 A (FUKUI et al) 21 November 1989, entire document.	1-16 and 33-38
X	US 5,234,712 A (HOWARD) 10 August 1993, entire document.	1-5, 10-22, 28-43 and 48-52

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

•	Special categories of cited documents:	•T	later documents published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
•A	document defining the general state of the art which is not considered to be of particular relevance		
•E	earlier document published on or after the international filing date	•X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
•L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	•Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
•O	document referring to an oral disclosure, use, exhibition or other means		
•P	document published prior to the international filing date but later than the priority date claimed	•A	document member of the same patent family

Date of the actual completion of the international search

15 DECEMBER 2000

Date of mailing of the international search report

26 FEB 2001

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